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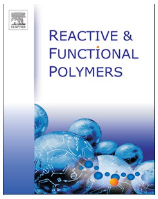

Concomitant cationic polymerization of a hybrid monomer and an epoxy resin

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ABSTRACT

The concomitant cationic polymerization of an epoxy resin and a hybrid monomer is a new concept for toughening epoxy resins. Thermolatent super acids are superior initiators of twin monomer polymerization and copolymerization. Determination of gel yield and instrumental characterization of the formed complex polymer network indicate that copolymerization occurs, integrating the linear silicone and novolak formed during twin polymerization into the epoxy network.

1. Introduction

Phenolic resins (especially novolaks) have high thermal stability, excellent aging resistance, and low flammability [1]. Thus, these materials are used in the aeronautics and automotive industries and are still being improved [2,3]. Unfortunately, these materials have two main drawbacks: brittleness and the requirement of curing under severe conditions [4]. The curing conditions for phenolic resins were first illustrated by the “heat and pressure” patent of Baekeland [5]. To overcome the drawbacks of phenolic resins, toughening with silicones has been investigated [6]. To achieve high impact strength, phase separation in the nano-range appears to be a promising concept that might be feasible with new polymerization methods.

Spange et al. have recently developed a new type of polymerization method: twin polymerization [7]. This template-free method can be used to generate organic–inorganic nanocomposites [8,9]. In twin polymerization, a so-called hybrid monomer (or twin monomer) simultaneously forms two interpenetrating but independent homopolymers via acidic catalysis [7,10–13]. This coupled polymerization mechanism causes time synchronization of the homopolymer formation, which might be the reason for the formation of a nanoscopic interpenetrating network with domain sizes in the range of 0.5–3 nm [11]. Domain sizes of this dimension have not been realized using conventional simultaneous polymerization of two different monomers. Certain hybrid monomers such as 2,2′-spirobi[4*H*-1,3,2-benzodioxasiline] (SBS) and 2,2-dimethyl-4*H*-1,3,2-benzodioxasiline (DBS) **(1)** have cyclic structures that avoid condensation products such as water during novolak formation. These cyclic hybrid monomers connect their polymerizable components by two different reactive bridges that break up consecutively [11]. Spange et al. suggest that there is a covalent connection between both components during the entire reaction until the polymers have formed.

Simultaneous conversion of two hybrid monomers leads to either a simultaneous twin polymer or a simultaneous twin copolymer [14]. Löschner et al. suggest that 2,2-dimethyl-4*H*-1,3,2-benzodioxasiline (DBS) **(1)** can be a potential hybrid monomer for simultaneous twin polymerization, forming a novolak and poly(dimethyl siloxane) (PDMS). This concomitant novolak and PDMS formation is proposed as an effective toughening method for the novolak. In addition, epoxy resins can be toughened by silicones [6,15] and, via cationic polymerization, possibly also by the novolak whose hydroxyl group most likely reacts via the activated monomer mechanism [16,17].

Cationically polymerized epoxy resins are widely used for technical applications such as adhesives, electrical insulators, printing inks, and coatings due to their high modulus, high glass transition temperature, and good chemical resistance. To reduce the brittleness of such epoxy resins, thermoplastics with hydroxyl groups can be incorporated via a chain transfer reaction known as the activated monomer mechanism (AM) [16–20]. Compared with the activated chain-end mechanism (ACE), which describes chain

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growth of the epoxy resin by reaction of the chain with another epoxide, the activated monomer mechanism leads to chain termination with simultaneous initiation of a new chain. Recently, it has been demonstrated that crystallizable polymeric alcohols such as poly(ε-caprolactone) are efficient toughening agents [21]. For the formation of crystalline thermosets with superior mechanical properties, effective nucleation is the crucial step [22].

Epoxide polymerization can be cationically initiated by photolatent diaryliodonium and triarylsulfonium salts [23,24] or by thermolatent initiators based on benzyl sulfonium salts with different counterions such as BF_4^-, PF_6^-, AsF_6^-, and SbF_6^- [25–27]. These latent initiators form a super acid or a carbocation during thermal or photochemical decomposition, which effectively initiates epoxide polymerization.

There are unanswered questions about whether the cationic twin polymerization can be initiated by latent initiators, whether concomitant polymerization of a hybrid monomer with an epoxy resin is possible, and what structures are formed in such a complex reaction.

In this work, we investigate the cationic twin polymerization of 2,2-dimethyl-4*H*-1,3,2-benzodioxasiline **(1)** with the thermolatent initiator benzyl tetrahydrothiophenium hexafluoroantimonate **(3),** which is known to initiate epoxide polymerization. Furthermore, the concomitant polymerization of a hybrid monomer **(1)** and the epoxy resin 3,4-epoxycyclohexyl-3′,4′-epoxycyclohexane carboxylate **(2)** in the presence of the latent initiator **(3)** is examined.

2. Experimental

2.1. Materials

All chemicals were used as received from commercial suppliers unless otherwise specified. Toluene, methanol, and triethylamine were purchased from Sigma Aldrich (Schnelldorf, Germany). Toluene was dried before use and stored under an argon atmosphere. Triethylamine was distilled and stored under an argon atmosphere. Dimethyldichlorosilane was obtained from ABCR (Karlsruhe, Germany). Salicyl alcohol and trifluoroacetic acid (99%) were purchased from Alfa Aesar (Karlsruhe, Germany). The cycloaliphatic epoxide 3,4-epoxycyclohexyl-3′,4′-epoxycyclohexane carboxylate **(2)** (Omnilane OC1005) was purchased from IGM resins (Krefeld, Germany). The latent initiator benzyl tetrahydrothiophenium hexafluoroantimonate **(3)** was prepared according to Endo et al. [27].

2.2. Physico-chemical characterization

Infrared spectra were measured in attenuated total reflection (ATR) mode using a Bruker Equinox 55 FTIR-spectrometer equipped with a Golden Gate cell with a resolution of 4 cm^{-1}. ^1H and ^{13}C NMR spectra were recorded with a Bruker DPX-200 spectrometer. Tetramethylsilane was used as the external standard. The spectra were recorded in $CDCl_3$ or in d_6-acetone at room temperature. DSC measurements were performed in a sealed pan on a DSC 2920 Modulated system from TA Instruments in the temperature range from 20 °C to 250 °C at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed on a Q5000 system from TA Instruments. The measurements were performed in flowing air from 20 °C to 600 °C at a heating rate of 10 °C/min. Dynamic mechanical analysis (DMA) was performed on a DMA 2980 instrument from TA Instruments. A heating rate of 2 °C/min was used in the range from −50 °C to 270 °C.

2.3. Synthesis

*2.3.1. 2,2-dimethyl-4H-1,3,2-benzodioxasiline (DBS) **(1)***

In total, 18.6 g (0.15 mol) of salicyl alcohol was placed in a dry glass system under an argon atmosphere consisting of a 500-mL three-necked round bottom flask, a stirrer, a reflux condenser, and a dropping funnel. Next, 250 mL dry toluene was added and stirred until the diol was completely dissolved. Then, 48.5 mL (0.35 mol) distilled triethylamine and then a small excess of dimethyldichlorosilane (24.4 mL; 0.20 mol) were added dropwise. After stirring at 80 °C for 3 h, the solution was stirred for an additional 12 h at room temperature. The resulting solid triethylammonium chloride was filtered off on a glass frit under an argon atmosphere and then washed with 70 mL dry toluene. The solvent was then removed under vacuum. Finally, the product was distilled from the residue under reduced pressure (31–32 °C; 4.2×10^{-2} mbar). In total, 16 mL (71% of the theoretical yield) of 2,2-dimethyl-4*H*-1,3,2-benzodioxasiline **(1)** was obtained as a colorless transparent liquid and was stored under inert conditions [30]:

> *^{1}H NMR ($CDCl_3$)*: δ [ppm] = 0.38 (s, 6H, CH_3); 4.97 (s, 2H, $O{-}CH_2$); 6.91–7.28 (m, 4H, aromatic C—H).
> *^{13}C NMR ($CDCl_3$)*: δ [ppm] = 1.43 (2C, $Si{-}CH_3$); 63.78 (1C, CH_2); 119.30, 121.01, 126.36 and 128.93 (1C, aromatic C—H); 127.06 and 153.13 (1C, aromatic C_q).
> *ATR-IR*: ν [cm^{-1}] = 1606, 1581 and 1485 m ($\nu_{C{=}C}$, aromatic), 1255 vs ($\nu_{Si{-}C{-}H}$, $Si{-}CH_3$), 1230 m ($\nu_{aryl{-}O}$, $C_{aromatic}{-}O$), 1030 s ($\nu_{aryl{-}O{-}C}$, $C_{aromatic}{-}O{-}CH_2$), 908 vs ($\nu_{Si{-}O{-}aryl}$, $Si{-}O{-}C_{aromatic}$), 861 s ($\nu_{Si{-}C{-}H}$, $Si{-}CH_3$), 838 s ($\nu_{aryl{-}O{-}C}$, $C_{aromatic}{-}O{-}CH_2$).

*2.3.2. Twin polymerization of 2,2-dimethyl-4H-1,3,2-benzodioxasiline **(1)***

2.3.2.1. Trifluoroacetic acid as initiator. In total, 0.068 g (0.60 mmol) trifluoroacetic acid was placed in a 5-mL round bottom flask fitted with a reflux condenser. Then, 2 mL (11.9 mmol) of hybrid monomer **(1)** was added dropwise. The apparatus was purged with argon, and the solution was heated at 85 °C bath temperature for four hours under stirring. A turbid milky orange solid was obtained.

*2.3.2.2. Benzyl tetrahydrothiophenium hexafluoroantimonate **(3)** as initiator.* In total, 0.125 g (0.3 mmol) benzyl tetrahydrothiophenium hexafluoroantimonate **(3)** was placed in a 5-mL round bottom flask fitted with a reflux condenser. Then, 0.136 g acetone was added under stirring to dissolve the latent initiator. Next, 1 mL (5.93 mmol) of the hybrid monomer **(1)** was added dropwise to the solution. The apparatus was purged with argon and refluxed for four hours under stirring. Finally, the solution was heated at 120 °C bath temperature to evaporate the acetone and to complete the polymerization. A red-brown solid was formed.

*2.3.3. Simultaneous twin polymerization of 2,2-dimethyl-4H-1,3,2-benzodioxasiline **(1)** and 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate **(2)***

Concomitant polymerizations of both monomers **(1)** and **(2)** were performed in different ratios as indicated in Table 1. The initiator benzyl tetrahydrothiophenium hexafluoroantimonate **(3)** was dissolved in the diepoxide **(2)** by mixing for 10 min with a speedmixer (DAC 150 FVZ, Hauschild & Co. KG, Hamm, Germany). Then, the hybrid monomer **(1)** was added, and the solution was again homogenized with a speedmixer (30 s). A few drops of methanol were added to samples 0/10 to 4/6, in which the initiator **(3)** was not sufficiently soluble without a minimum of solvent. The reactive mixtures were poured into a silicone mold with dimensions of $34 \times 10 \times 3$ mm^3 and then polymerized in a pre-heated oven at 100 °C for two hours. For post-curing, the samples were heated at 150 °C for another three hours after removal from the mold.